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FERROELECTRIC PROPERTIES OF POLY (VINYLIDENE FLUORIDE) TETRAFLUOR--ETC(U)
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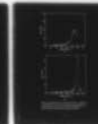
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Technical Report 188

**FERROELECTRIC PROPERTIES OF
POLY(VINYLIDENE FLUORIDE—
TETRAFLUOROETHYLENE)**

JC Hicks, TE Jones and JC Logan

1 January 1978

Final Report: October 1976 - November 1977

Prepared For:
Technical Director, NOSC
and Naval Material Command

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The work reported herein was performed from October 1976 to November 1977. It was supported jointly by the Independent Research and Exploratory Development program at the Naval Ocean Systems Center and by the Naval Material Command (NMAT-08T21) under Transduction Science Block funds.

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Advanced Concepts Division

Under authority of
DA Kunz, Head
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ACKNOWLEDGEMENTS

The authors wish to thank Dr. Eric J. Lind for his assistance in designing the apparatus for measuring the piezoelectric stress coefficients and Dr. G. Thomas Davis for several valuable discussions.

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NOSC/TR-188	2. GOVT ACCESSION NO.	3. DATE OF REPORT & PERIOD COVERED Final report Oct 76 - Nov 77,
4. TITLE (and Subtitle) Ferroelectric Properties of Poly (vinylidene fluoride-tetrafluoroethylene)	5. AUTHOR(s) J. C. Hicks, T. E. Jones, J. C. Logan	6. PERFORMING ORG. REPORT NUMBER Final Report October 1976 - November 1977
7. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Ocean Systems Center San Diego, CA 92152	8. CONTRACT OR GRANT NUMBER(s)	10. PROGRAM ELEMENT PROJECT, TASK AREA & WORK UNIT NUMBERS 62766N and 61152N
11. CONTROLLING OFFICE NAME AND ADDRESS Technical Director, NOSC, and Naval Material Command Washington, D.C. 20360	12. NUMBER OF PAGES 16	15. SECURITY CLASS. (of this report) UNCLASSIFIED
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15a. DECLASSIFICATION DOWNGRADING SCHEDULE	16. DISTRIBUTION STATEMENT (of this Report) Approved for public release, distribution unlimited.
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)	18. SUPPLEMENTARY NOTES	
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) piezoelectric polymers polyvinylidene fluoride		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Ferroelectric hysteresis of a copolymer of vinylidene fluoride with tetrafluoroethylene and of uniaxially-stretched polyvinylidene fluoride has been observed at 60 Hz at room temperature. The measured remanent polarization of the copolymer was in good agreement with a calculated value using a frozen dipole model and measured piezoelectric coefficients. The dielectric constant for the copolymer has been measured at 1000 Hz as a function of temperature and a large peak which may be interpreted as occurring at the Curie temperature appears		

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at 122°C. Also, a set of copolymer films of varying thickness were poled above the Curie temperature and their piezoelectric stress coefficients, g_{31} , were measured as a function of the poling field. These measurements indicate that the copolymer, when poled above the Curie temperature, exhibits bulk polarization. All of these results suggest that this copolymer is ferroelectric and that poling aligns the dipoles in the β crystal phase of the material.

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SUMMARY

The origin of the large piezoelectric coefficients that have been observed in polyvinylidene fluoride is not yet completely understood. In order to gain some insight into the origin of these coefficients, the ferroelectric hysteresis of a copolymer of vinylidene fluoride with tetrafluoroethylene and of uniaxially-stretched polyvinylidene fluoride was observed at 60 Hz at room temperature. The measured remanent polarization of the copolymer was in good agreement with a calculated value using a frozen dipole model and measured piezoelectric coefficients. The dielectric constant for the copolymer was measured at 1000 Hz as a function of temperature and a large peak which may be interpreted as occurring at the Curie temperature appears at 122°C. Also, a set of copolymer films of varying thickness were poled above the Curie temperature and their piezoelectric stress coefficients, g_{31} , were measured as a function of the poling field. These measurements indicate that the copolymer, when poled above the Curie temperature, exhibits bulk polarization. All of these results suggest that this copolymer is ferroelectric and that poling aligns the dipoles in the β crystal phase of the material.

An additional experiment is being planned to measure the remanent polarization observed in the hysteresis as a function of the maximum electric field across the polymer film and then measure their respective piezoelectric coefficients, g_{31} , to determine the correlation between the remanent polarization, P_r , and the piezoelectric coefficient, g_{31} .

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CONTENTS

INTRODUCTION	3
EXPERIMENTAL	4
RESULTS	6
DISCUSSION	9
CONCLUSION	12
REFERENCES	13
APPENDIX	15

INTRODUCTION

The large piezoelectric coefficients in polarized polyvinylidene fluoride (PVDF) have stimulated a great deal of interest in this polymer since its discovery.¹ Numerous investigators have measured the magnitude of these coefficients under different poling conditions²⁻⁸ as well as their thermal stability as a function of temperature.^{5,6} In addition, piezoelectric coefficients have been measured as a function of bias field.^{9,10} These investigations, combined with morphology studies,¹¹⁻¹⁵ thermally stimulated discharge and pyroelectric measurements,¹⁶⁻²² observations of optical second harmonic generation,¹⁶ and studies of ferroelectric-like hysteresis,^{9,21} have led to only a partial understanding of the mechanisms responsible for the large piezoelectric coefficients and ferroelectric-like properties. A complete understanding of these phenomena must, of course, wait until the microscopic mechanisms responsible for these effects can be directly identified and measured.

The purpose of this work is to better understand the origin of the electrical properties of a copolymer of vinylidene fluoride and tetrafluoroethylene. To accomplish this, the charge induced on the surface of the copolymer was measured as a function of the electric field at room temperature, the dielectric constant was measured as a function of temperature, and the piezoelectric coefficients of films of various thicknesses were measured as a function of the poling field.

EXPERIMENTAL

A commercially available copolymer of vinylidene fluoride-tetrafluoroethylene, P(VDF-TFE), containing 27% tetrafluoroethylene was chosen for our investigations. The advantage of using this copolymer is that it crystallizes directly from the melt into a crystal phase analogous to that of the β phase of the PVDF homopolymer. This eliminates the mechanical drawing step which is required in PVDF to transform the α to the β phase, and there is no preferred orientation in our P(VDF-TFE) films. However, this is probably not the optimum copolymer, as such a high percentage of tetrafluoroethylene reduces the number of dipoles per unit volume and the maximum possible crystallinity. Furthermore, 27% tetrafluoroethylene is the concentration with the lowest melting temperature, 126°C, which should have an adverse effect on the thermal stability.

The copolymer powder, P(VDF-TFE), was of commercial grade and was filtered through wire mesh sieves of 60-micron pore size to eliminate some of the impurities. Then the polymer powder was placed in a stainless steel die and heated to 180°C in vacuum. The resulting plug was pressed between polished nickel-plated stainless steel platens with a pressure of 1000 newtons/cm² at 180°C. The resulting films were then cooled in the press under pressure to room temperature over a period of approximately 30 minutes. To vary the thickness of the films, shims of 100, 200, and 300 microns were used at the edge of the platens. In addition, a 25-micron-thick copolymer film with a 2:1 draw ratio was obtained from Pennwaldt Corporation.

After thoroughly cleaning the films in a high strength detergent and rinsing in deionized filtered water, aluminum electrodes (5 cm x 10 cm) with offset tabs were vacuum deposited on the films. Adhesion of the aluminum to the copolymer was excellent when proper surface cleaning and good vacuum technique was used. Copper leads were used for the poling process and for the hysteresis measurements and were attached to the tabs with Indium solder.

For poling, the films were placed in a support which was immersed in a circulating dielectric grade silicone oil bath. The films were poled at 130 \pm 1°C. The temperature was monitored with a digital thermometer using an Iron-Constantan thermocouple. Poling times were 30 minutes with approximately a 20-minute cooling cycle.

For the hysteresis studies, a circuit similar to a Sawyer-Tower circuit²³ is used, as shown in figure 1. During these studies, the films remained in the oil bath to avoid heating and the consequent dielectric fatigue.

For the dielectric constant measurements, the films again remained in the oil bath and the dielectric constant and loss were measured at 1000 Hz with an impedance bridge.

The piezoelectric stress coefficient, g_{31} , was measured using the circuits and instrumentation shown in figure 2, where the 1 and 2 axes lie in the plane of the film and the 3 axis is perpendicular to the film.

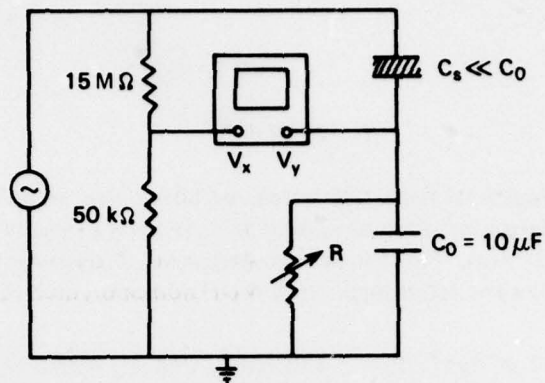


Figure 1. Sawyer-Tower circuit used for measuring D versus E . C_0 is the standard capacitor for measuring the electric displacement, D , and R is the variable resistor for canceling dielectric loss.

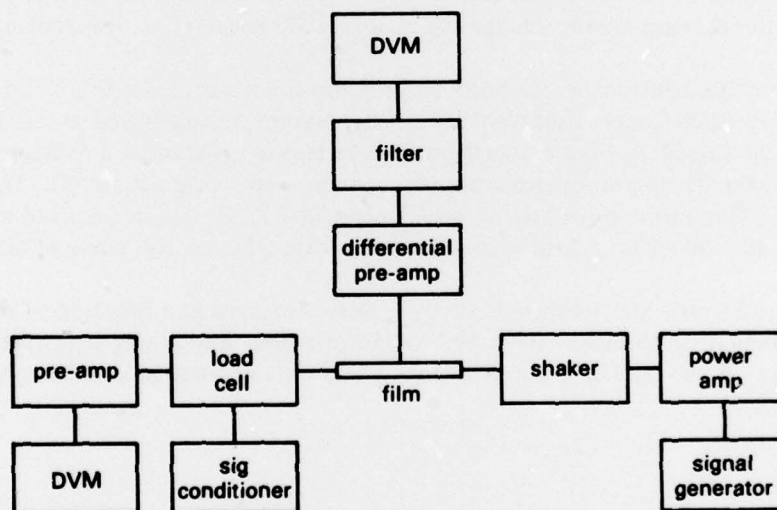


Figure 2. Schematic diagram of the apparatus used for measuring the piezoelectric stress coefficient, g_{31} .

RESULTS

When a high sinusoidal field, 825 kv/cm, of 60 Hz was applied to the 25-micron copolymer sample, a ferroelectric hysteresis of D versus E was observed at room temperature as shown in figure 3(a). The remanent polarization, P_r , saturation polarization, P_s , and coercive field, E_c , were determined from the D versus E curve ($D = \epsilon_0 E + P$);

$$P_r = 2.1 \mu\text{C}/\text{cm}^2, P_s = 2.4 \mu\text{C}/\text{cm}^2, \text{ and } E_c = 365 \text{ kv}/\text{cm}.$$

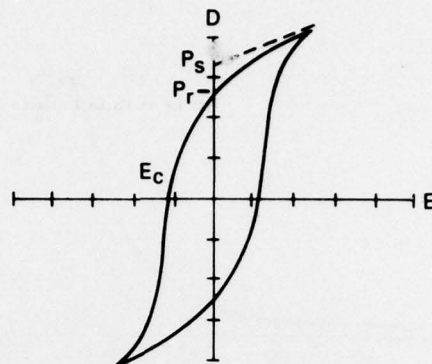
Similar ferroelectric hysteresis was observed for the PVDF homopolymer film of 27-micron thickness obtained commercially from Kreha Corporation of America. This hysteresis is shown in figure 3(b). With a maximum field of 1200 kv/cm, the remanent polarization, saturation polarization, and coercive field obtained from this curve are

$$P_r = 2.4 \mu\text{C}/\text{cm}^2, P_s = 3.4 \mu\text{C}/\text{cm}^2, \text{ and } E_c = 345 \text{ kv}/\text{cm}.$$

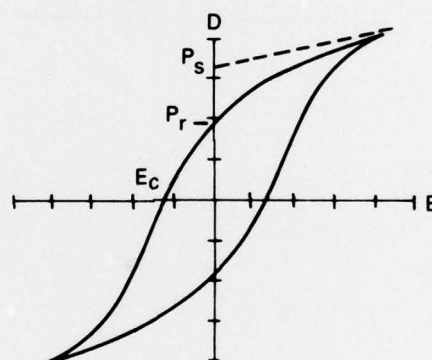
Note the much "harder" hysteresis for the copolymer as compared to the homopolymer. Even with a smaller saturation electric field, the copolymer has a larger coercive field. Also, the ratio of the remanent polarization to the saturation polarization is larger for the copolymer as compared to the homopolymer, 0.88 versus 0.71, respectively.

The dielectric constant, ϵ , for both a 25-micron-thick sample (with a 2:1 draw ratio) and a 100-micron-thick sample (undrawn) of the copolymer was measured as a function of temperature at 1000 Hz. Figure 4(a) shows the dielectric constant as a function of temperature for the 25-micron-oriented sample, and the peak occurs at 109°C. The peak in $\epsilon(T)$ for the 100-micron sample, figure 4(b), occurs at 122°C. These values of $\epsilon(T)$ agree quite well with the low electric field values obtained from a D versus E curve at 60 Hz.

The piezoelectric stress coefficients, g_{31} , were measured as a function of the poling field for films ranging in thickness from 100 to 250 microns. The poling temperature was 130°C which was above the Curie temperature. The results of these measurements are given in figure 5.

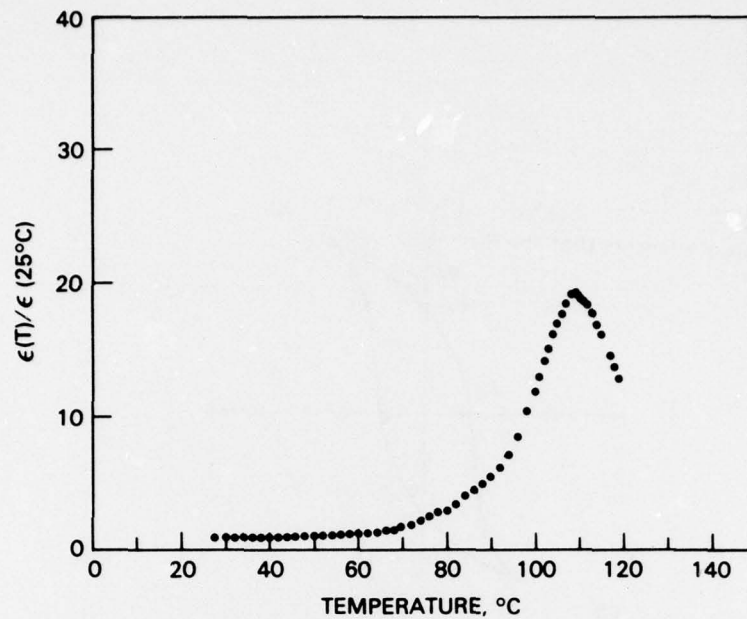


(a)

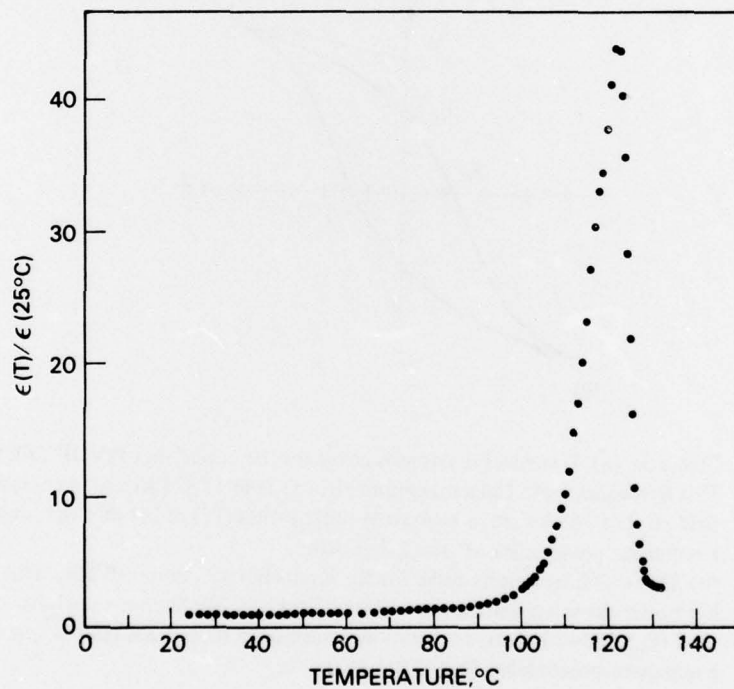


(b)

Figure 3. (a) D versus E hysteresis curve for the copolymer P(VDF-TFE). This hysteresis curve has a maximum electric field of 825 kv/cm, a coercive field (E_c) of 365 kv/cm, a saturation polarization (P_s) of $2.4 \mu\text{C}/\text{cm}^2$, and a remanent polarization (P_r) of $2.1 \mu\text{C}/\text{cm}^2$. (b) D versus E hysteresis curve for the Kreha homopolymer PVDF. This hysteresis curve has a maximum electric field of 1200 kv/cm, a coercive field (E_c) of 345 kv/cm, a saturation polarization (P_s) of $3.4 \mu\text{C}/\text{cm}^2$, and a remanent polarization (P_r) of $2.4 \mu\text{C}/\text{cm}^2$.



(a)



(b)

Figure 4. (a) Relative dielectric constant versus temperature, $\epsilon(T)/\epsilon(25^\circ\text{C})$, for an oriented (2:1 draw ratio) 25-micron-thick copolymer, P(VDF-TFE). (b) Relative dielectric constant versus temperature, $\epsilon(T)/\epsilon(25^\circ\text{C})$, for a randomly-oriented 100-micron-thick copolymer, P(VDF-TFE).

DISCUSSION

The ferroelectric hysteresis observed in the Kreha film and the copolymer, figures 3(a) and 3(b), strongly suggests that the β -phase crystal is ferroelectric. The remanent and saturation polarization compares favorably with the results from a relatively simple model for frozen dipoles. It has been shown for this model²⁴ that the polarization for a single crystal is given by:

$$P = \frac{\epsilon_{\infty} + 2}{3} \left(\frac{N\mu_0}{V} \right) \langle \cos \theta \rangle; \quad (1)$$

where P = polarization,
 ϵ_{∞} = high frequency dielectric constant,
 N/V = number of dipoles per unit volume,
 μ_0 = dipole moment of the monomer unit, and
 $\langle \cos \theta \rangle$ = average value of the cosine of the angle between the dipole moment and the polarization.

For the copolymer, the appropriate expression for the remanent polarization is

$$P_r = \frac{\epsilon_{\infty} + 2}{3} \left(\frac{N\mu_0}{V} \right) \langle \cos \theta \rangle_r X_1 X_2 X_3; \quad (2)$$

where X_1 = mole fraction of sample which is vinylidene fluoride, 0.73,
 X_2 = mole fraction of sample which is crystalline, 0.40, and
 X_3 = mole fraction of polymer chain which has head to tail addition, 0.95.

The number of dipoles per unit volume, N/V , is calculated from lattice constants determined from x-ray diffraction patterns on a similar copolymer²⁵ containing 7% tetrafluoroethylene. The lattice constants are $a = 8.85 \text{ \AA}$, $b = 5.00 \text{ \AA}$, and $c = 2.55 \text{ \AA}$ with 2 dipoles per unit cell. The carbon-fluorine bond has a dipole moment of 2.1 Debyes, and the high frequency dielectric constant, ϵ_{∞} , is equal to 3. Substituting these values into equation (2) yields

$$P_{r,s} = 5.7 \langle \cos \theta \rangle_{r,s} \mu\text{coul/cm}^2, \quad (3)$$

where $P_{r,s}$ represents either the remanent or the saturation polarization, as appropriate.

Applying this model to our data, we obtain from figure 3(a), $\langle \cos \theta \rangle_r = 0.37$ and $\langle \cos \theta \rangle_s = 0.42$. A similar calculation for the homopolymer with lattice constants $a = 8.58 \text{ \AA}$, $b = 4.91 \text{ \AA}$, and $c = 2.56 \text{ \AA}$ ²⁶ and a crystallinity of 0.5 yields

$$P_{r,s} = 6.5 \langle \cos \theta \rangle_{r,s} \mu\text{coul/cm}^2. \quad (4)$$

On the basis of this model, we obtain $\langle \cos \theta \rangle_r = 0.37$ and $\langle \cos \theta \rangle_s = 0.52$.

These values for $\langle \cos \theta \rangle$ are reasonable if one assumes that during poling the only mechanism for aligning dipoles is a 180° rotation of the polymer chain about its axis. Then the maximum value of $\langle \cos \theta \rangle$ expected for a randomly oriented sample is 0.5.

Another interesting comparison of this model with experiment is the calculation of the hydrostatic piezoelectric strain coefficient, d_h ,²⁷ which is

$$d_h = \frac{1}{A} \frac{dQ}{dp} = -P \epsilon_\infty \beta_L, \quad (5)$$

where β_L is the linear compressibility.

The measured values of d_h and β_L ²⁷ for this copolymer yield:

$$P = 1.92 \text{ } \mu\text{coul/cm}^2. \quad (6)$$

This is in good agreement with our measured value of $P_r = 2.10 \text{ } \mu\text{coul/cm}^2$.

The observed peaks, figures 4(a) and 4(b), in the dielectric constant are interesting in that they are indicative of a phase transformation from a ferroelectric to a paraelectric state.²⁸ With this interpretation, the peaks occur at the Curie temperature. For both the drawn and undrawn samples, the Curie temperature occurs below the melt temperature. The differences in figures 4(a) and 4(b) are substantial in that the peaks occur at different temperatures, the peaks have different widths at half maximum, and their peak values are different. These differences are very likely due to the internal strains in the oriented sample. The stress dependence of the Curie temperature for both ferromagnetic²⁹ and ferroelectric³⁰ materials is well documented. Furthermore, the observed remanent polarization decreased continuously as this temperature was approached from below.

The observed independence of the piezoelectric stress coefficient, g_{31} , as a function of thickness for the unoriented copolymer is shown in figure 5. These films were all poled at 130°C which is above the Curie temperature. The data indicate that the poling was uniform and this is consistent with a bulk phenomenon and ferroelectricity. It is interesting to note that the thicker films appear to have a slightly higher g_{31} for the same poling fields. This is due to the larger thickness ratio of copolymer to aluminum for the thicker samples, thereby reducing the relative stiffness increase caused by the aluminum layer on the surface.

In a thermal pulse experiment, the thermally-stimulated charge given off by this copolymer has been measured as a function of time for two different poling temperatures.³¹ The spatial distribution of the polarization can be determined from this data using a method described in the literature.³² These spatial distributions³¹ indicate that increasing the poling temperature leads to more uniform poling through the thickness of the material, which is in good agreement with our results.

An alternate model which has been proposed to explain the electrical activity of the vinylidene-fluoride polymers is charge injection. This model has been invoked to explain the results of certain "sandwich" experiments.^{4,17,33} These experiments involve attempts to pole PVDF in an arrangement which usually has a layer of Mylar separating a layer of PVDF from the poling electrodes. In each experiment the electric poling field in the PVDF is calculated by using a simple capacitance model with low electric field and room temperature values of the respective dielectric constants. It is clear from the data presented here, that the dielectric constant for a related copolymer is strongly dependent upon both the electric field and temperature, and we expect the homopolymer to show a similar dependence. Therefore, these room temperature and low-electric field values of the dielectric constants do not, in fact, represent the true value of these dielectric constants during poling. Furthermore, the problem is even more complicated than this, since at high poling temperatures and fields there are substantial leakage currents; and it is the conductivities which eventually determine how the electric fields divide in such a "sandwich" arrangement (see appendix). Therefore, these experiments must be considered in much more detail before their results can be interpreted correctly.

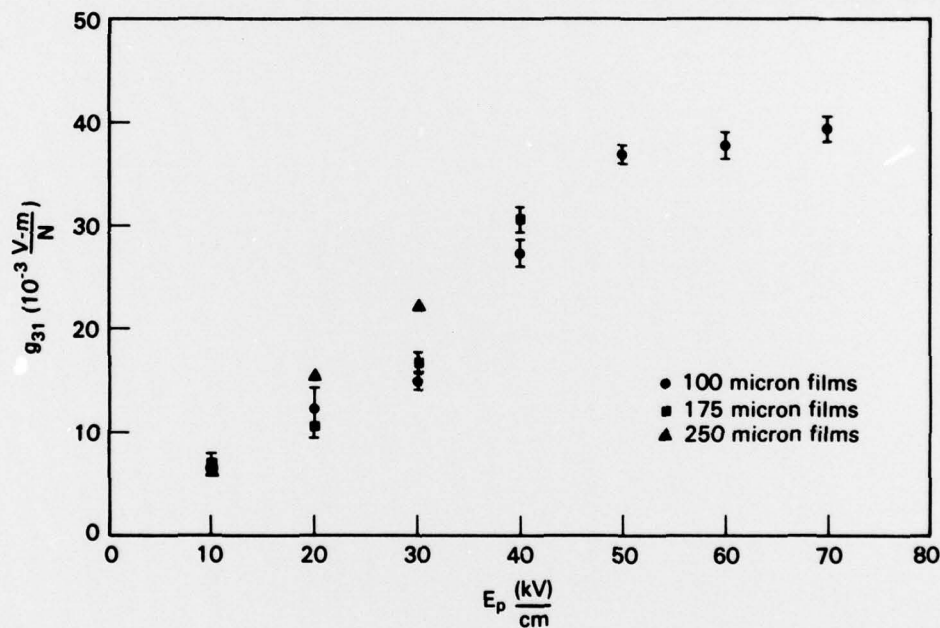


Figure 5. Piezoelectric stress coefficients, g_{31} , as a function of the poling field for films ranging in thickness from 100 to 250 microns.

CONCLUSION

We have studied the copolymer, P(VDF-TFE), which is known to be both piezoelectric and pyroelectric.²⁷ These are both necessary, but not sufficient, properties for any substance to be termed ferroelectric. We have measured the polarization hysteresis, D versus E , for unpoled samples of this copolymer and the resulting hysteresis exhibits reversible polarization. The fact that the copolymer exhibits reversible remanent polarization, along with its observed piezoelectric and pyroelectric properties, forces us to conclude that it is truly ferroelectric. The origin of the ferroelectricity is the dipole moment of each monomer ($\text{CH}_2 = \text{CF}_2$) unit, and the fact that this copolymer crystallizes into a polar (β) crystal phase. The values obtained from the hysteresis figures, for both the saturation and the remanent polarization, are in excellent agreement with the values calculated from a dipole model, using the known dipole moment of the $\text{CH}_2 = \text{CF}_2$ monomer and the measured crystal parameters. Furthermore, a sharp peak was observed in the dielectric constant at the Curie temperature and the observed remanent polarization decreased continuously as this temperature was approached from below.

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APPENDIX

Consider two uniform dielectrics "sandwiched" together between electrodes. The dielectrics will have, respectively, thicknesses t_1 and t_2 , relative dielectric constants ϵ_1 and ϵ_2 , and conductivities σ_1 and σ_2 . At time $t = 0$, a voltage V_0 is placed across the two electrodes. To calculate the electric fields, E_1 and E_2 , as a function of time in the two dielectrics, consider Maxwell's equation

$$\nabla \cdot D = \rho_f, \quad (A-1)$$

and the equation of continuity

$$\nabla \cdot j + \frac{\partial \rho_f}{\partial t} = 0, \quad (A-2)$$

with the boundary condition

$$E_1 t_1 + E_2 t_2 = V_0, \quad (A-3)$$

where ρ_f is any free charge trapped within the dielectric. For any uniform dielectric, the trapped free charge will occur at the interface, therefore $\rho_f = \Sigma \delta(x-t_2)$, where Σ is the surface charge density at the interface and δ is the Dirac delta function. Defining the current densities as j_1 and j_2 , respectively, equations (A-1) and (A-2) become

$$\frac{\partial}{\partial x} (\epsilon_2 E_2 + (\epsilon_1 E_1 - \epsilon_2 E_2) \theta(x-t_2)) = \Sigma \delta(x-t_2), \quad (A-4)$$

and

$$\frac{\partial}{\partial x} (j_2 + (j_1 - j_2) \theta(x-t_2)) + \frac{\partial}{\partial t} \Sigma \delta(x-t_2) = 0, \quad (A-5)$$

where θ is the unit step function. These two equations readily simplify to

$$\epsilon_1 E_1 - \epsilon_2 E_2 = \Sigma(t), \quad (A-6)$$

and

$$\sigma_2 E_2 - \sigma_1 E_1 = \frac{\partial \Sigma}{\partial t}, \quad (\text{A-7})$$

where $j = \sigma E$

Differentiating equation (A-6) with respect to time and equating to (A-7) yields

$$\epsilon_1 \frac{\partial E_1}{\partial t} + \sigma_1 E_1 = \epsilon_2 \frac{\partial E_2}{\partial t} + \sigma_2 E_2. \quad (\text{A-8})$$

Solving equation (A-8) with the boundary condition (A-3) yields

$$E_1 = \frac{\sigma_2 V_0}{\sigma_2 t_1 + \sigma_1 t_2} (1 - e^{-t/\tau}) + \frac{\epsilon_2 V_0}{\epsilon_2 t_1 + \epsilon_1 t_2} e^{-t/\tau}, \quad (\text{A-9})$$

and

$$E_2 = \frac{\sigma_1 V_0}{\sigma_2 t_1 + \sigma_1 t_2} (1 - e^{-t/\tau}) + \frac{\epsilon_1 V_0}{\epsilon_2 t_1 + \epsilon_1 t_2} e^{-t/\tau},$$

where $\tau = \frac{\epsilon_2 t_1 + \epsilon_1 t_2}{\sigma_2 t_1 + \sigma_1 t_2}.$

Therefore, at $t = 0$ the electric fields divide themselves so that the electric displacement, D , is continuous across the interface. Whereas, as t becomes much larger than τ the electric fields divide themselves so that the current density, j , is continuous across the interface.